INEEL/EXT-02-01109

Evaluation of the Hydraulic Performance and Mass Transfer Efficiency of the CSSX Process with the Optimized Solvent in a Single Stage of 5.5-Cm Diameter Centrifugal Contactor

J. D. Law
R. D. Tillotson
T. A. Todd

September 2002

Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

DISCLAIMER

INEEL/EXT-02-01109

Evaluation of the Hydraulic Performance and Mass Transfer Efficiency of the CSSX Process with the Optimized Solvent in a Single Stage of 5.5-Cm Diameter Centrifugal Contactor

Jack D. Law
Rich D. Tillotson
Terry A. Todd

September 2002

Idaho National Engineering and Environmental Laboratory
Environmental Research and Development Laboratory
Idaho Falls, Idaho 83415

Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Management
Under DOE Idaho Operations Office
Contract DE-AC07-99ID13727

ABSTRACT

The Caustic-Side Solvent Extraction (CSSX) process has been selected for the separation of cesium from Savannah River Site high-level waste. The solvent composition used in the CSSX process was recently optimized so that the solvent is no longer supersaturated with respect to the calixarene crown ether extractant. Hydraulic performance and mass transfer efficiency testing of a single stage of 5.5-cm ORNL-designed centrifugal contactor has been performed for the CSSX process with the optimized solvent. Maximum throughputs of the 5.5-cm centrifugal contactor, as a function of contactor rotor speed, have been measured for the extraction, scrub, strip, and wash sections of the CSSX flowsheet at the baseline organic/aqueous flow ratios (O/A) of the process, as well as at O/A's 20% higher and 20% lower than the baseline. Maximum throughputs are comparable to the design throughput of the contactor, as well as with throughputs obtained previously in a 5-cm centrifugal contactor with the non-optimized CSSX solvent formulation. The 20% variation in O/A had minimal effect on contactor throughput. Additionally, mass transfer efficiencies have been determined for the extraction and strip sections of the flowsheet. Efficiencies were lower than the process goal of ≥ 80%, ranging from 72 to 75% for the extraction section and from 36 to 60% in the strip section. Increasing the mixing intensity and/or the solution level in the mixing zone of the centrifugal contactor (residence time) could potentially increase efficiencies. Several methods are available to accomplish this including (1) increasing the size of the opening in the bottom of the rotor, resulting in a contactor which is partially pumping instead of fully pumping, (2) decreasing the number of vanes in the contactor, (3) increasing the vane height, or (4) adding vanes on the rotor and baffles on the housing of the contactor. The low efficiency results obtained stress the importance of proper design of a centrifugal contactor for use in the CSSX process. A prototype of any centrifugal contactors designed for future pilot-scale or full-scale processing should be thoroughly tested prior to implementation.

ACKNOWLEDGEMENTS

This work was supported by the U. S. Department of Energy, Office of Environmental Management, through the Tanks Focus Area of the Office of Science and Technology.

The authors wish to thank Tim Bronson of the INTEC Quality Control Laboratory for his assistance in solution and simulant makeup and Earlen Wade for his support in contactor setup, modification, and testing. Also, Peter Bonnesen of ORNL for providing the CSSX solvent for this testing and Ralph Leonard of ANL for his assistance in modeling of the centrifugal contactor and analysis of the data.

CONTENTS

FIGURES

TABLES

ACRONYMS

ANL	Argonne National Laboratory
BOBCalixC6	Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
CINC	Costner Industries Nevada Corp.
Cs-7SB	1-(2,2,3,3,-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol
CSSX	Caustic-Side Solvent Extraction
INEEL	Idaho National Engineering and Environmental Laboratory
ORNL	Oak Ridge National Laboratory
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TOA	Trioctylamine

Evaluation of the Hydraulic Performance and Mass Transfer Efficiency of the CSSX Process with the Optimized Solvent in a Single Stage of 5.5-Cm Diameter Centrifugal Contactor

INTRODUCTION

There are 34 million gallons of high-level waste requiring treatment at the Savannah River Site (SRS). As a part of this treatment process, the cesium will be removed from the waste, then vitrified for disposal. After the cesium is removed, the decontaminated solution will be immobilized as a low-level grout. The Caustic-Side Solvent Extraction (CSSX) process has been selected by the Department of Energy as the preferred alternative for cesium removal at the SRS.

The CSSX process was developed at Oak Ridge National Laboratory (ORNL) as a method to remove cesium from alkaline solutions such as DOE tank wastes at the SRS and Hanford, WA (Bonnesen et al. 1998). The CSSX solvent consists of (1) calix[4]arene-bis(*tert*-octylbenzo-crown-6), designated BOBCalixC6, for the extraction of cesium, (2) a modifier, 1-(2,2,3,3,-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB), to keep the extractant dissolved in the solvent and increase the ability to extract cesium in the extraction section, (3) trioctylamine (TOA), to suppress the effects from organic impurities so that the cesium can be back extracted from the solvent in the strip section, and (4) an Isopar® L diluent. In earlier development and testing of the CSSX process, the solvent composition was 0.01 $\underline{M}$ BOBCalixC6, 0.50 $\underline{M}$ Cs-7SB, and 0.001 $\underline{M}$ TOA in Isopar® L. Recently, the composition of the CSSX solvent has been optimized to 0.007 $\underline{M}$ BOBCalixC6, 0.75 $\underline{M}$ Cs-7SB, and 0.003 $\underline{M}$ TOA in Isopar® L (Klatt et al. 2002). With this change in composition, the CSSX solvent is no longer supersaturated with respect to the BOBCalixC6. The optimized solvent also has added resistance to third-phase formation at lower plant operating temperatures and to organic impurities that could limit back extraction of the cesium from the solvent. The density of the optimized solvent at 25°C increased from 810 to 852 g/L and the viscosity at 25°C increased from approximately 2.7 centipoise to 3.5 centipoise.

Testing was performed, prior to optimization of the CSSX solvent composition, to evaluate the hydraulic performance and mass transfer efficiency for the CSSX process in a 5-cm diameter centrifugal contactor (Birdwell and Anderson 2001). Since the optimized solvent has different physical properties than the previous solvent, the hydraulic performance of a centrifugal contactor may be affected. This created a need for additional hydraulic and mass transfer efficiency testing to be performed for the CSSX process using the optimized solvent.

Hydraulic and mass transfer efficiency testing for the CSSX process has been performed at the Idaho National Engineering and Environmental Laboratory (INEEL) using the optimized solvent and a single stage of 5.5-cm diameter centrifugal contactor. This testing consisted of (1) measurement of dispersion numbers for each of the flowsheet sections, (2) determination of the maximum throughput for the 5.5-cm contactor in each of the flowsheet sections, and (3) determination of the mass transfer efficiency of cesium in the extraction and strip sections. Results from this testing are presented in this report and compared to results obtained at ORNL with the prior solvent formulation.

EQUIPMENT DESCRIPTION

Measurement of dispersion numbers for each of the flowsheet sections was performed using standard laboratory glassware (100-mL graduated cylinders) and a stopwatch.

Hydraulic and mass transfer efficiency testing was performed using a single stage of an ORNL-designed 5.5-cm diameter centrifugal contactor four-pack. Table 1 lists the specifications of the contactor. The equipment is located in Lab 117 of building INTEC 637. A diagram of the experimental setup is shown in Figure 1 and photographs of the centrifugal contactor and experimental setup are shown in Figures 2 and 3. The speed of the centrifugal contactor was controlled from 0 to 4,400 rpm with a DC motor controller and verified during testing with a calibrated digital tachometer. Ten-liter Teflon® feed and product vessels were used for the solvent and ten-gallon high density polyethylene vessels were used for the aqueous solutions. All feed and product lines consisted of Teflon®-lined Tygon® tubing. Solution was pumped from the feed containers to the contactor stage using piston-type metering pumps (Fluid Metering Inc.). The solvent feed pump, model Q2V with dual pump heads Q2, has a maximum capacity of 2600 mL/min. Each pump head consisted of a stainless steel cylinder case, ceramic piston, and a ceramic cylinder liner. The aqueous feed pump, model Q2V with dual pump heads Q3, has a maximum capacity of 4600 mL/min. Each pump head consisted of a fluorocarbon (PVDF) cylinder case, ceramic piston, and a ceramic cylinder liner. Flow rates were adjusted by controlling pump speed using a ten-turn potentiometer or by manual adjustment of the piston stroke length and/or a combination of the two. Aqueous and organic solution exited the contactor stage and drained either to a receiver vessel (mass transfer efficiency tests) or back to the feed vessel (hydraulic performance tests). A tee in the drain lines with ball valves on the outlets provided a method for sampling the effluent streams. A thermocouple probe was inserted through the contactor drain line to a point just below the contactor mixing zone so that solution temperature inside the contactor stage could be monitored during operation.

Re-equilibration of the aqueous and organic samples from the mass transfer efficiency testing was accomplished using standard laboratory equipment and a temperature controlled water bath with a calibrated thermocouple. Temperatures of the solutions were maintained within the accuracy of the calibrated thermocouple (± 0.1ºC).

It should be noted that all glassware, plasticware, and solution vessels used for solution makeup or testing, as well as all wetted parts of the centrifugal contactor setup, were rinsed per the following procedure as recommended by ORNL.

1) Rinse 3 times with demineralized water
2) Rinse 3 times with ethanol
3) Rinse 3 times with acetone
4) Dry using an inert gas such as argon or nitrogen

Table 1. Specifications of the ORNL-designed 5.5-cm diameter centrifugal contactor.

Specification	Dimension
Rotor diameter	5.5 cm
Aqueous weir radius	12.70 mm
Organic weir radius	10.44 mm
Rotor inlet radius	7.89 mm
Aqueous underflow radius	22.71 mm
Height of separating zone below organic weir	109.0 mm
Height between weirs	18.26 mm
Rotor/housing gap	5.75 mm
Number of vanes below rotor	8
Inlet and outlet port configuration	Tangential

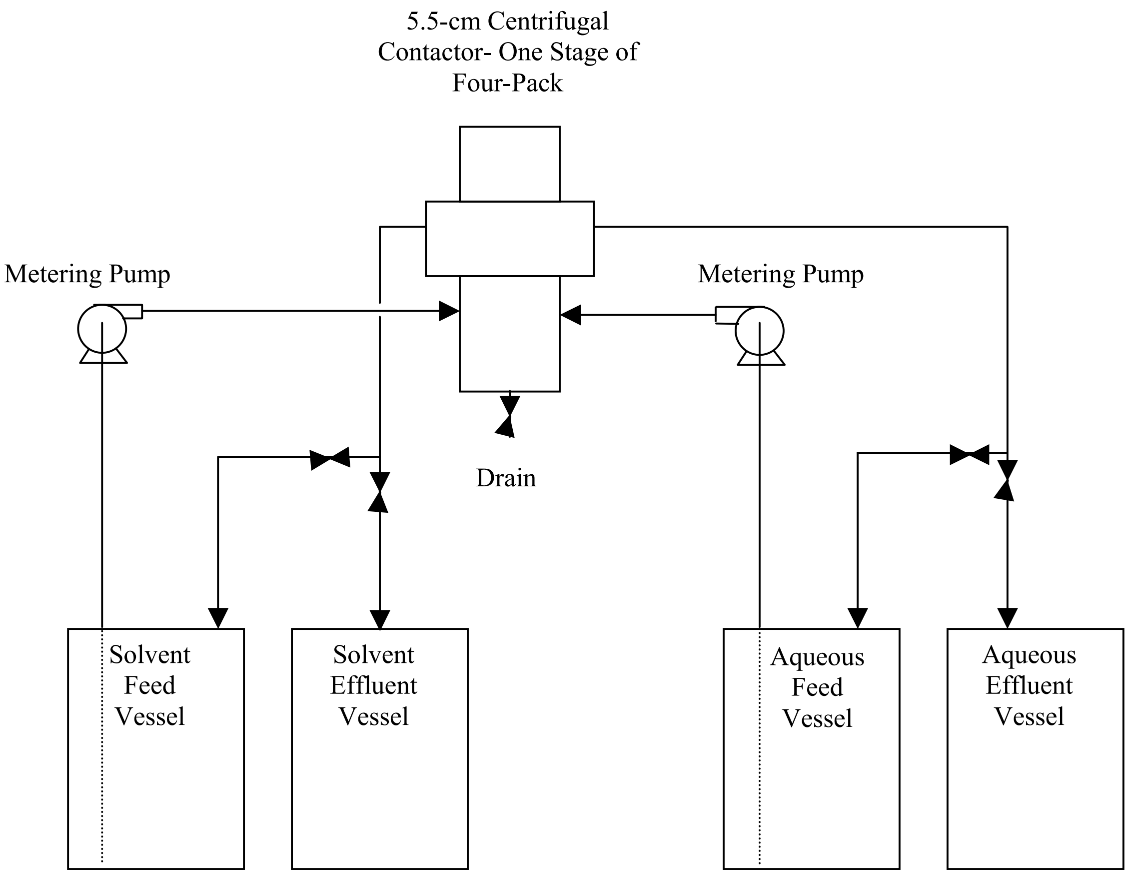

Figure 1. Experimental setup for contactor hydraulic and mass transfer efficiency tests.

Figure 2. 5.5-cm diameter centrifugal contactor test setup.

Figure 3. 5.5-cm centrifugal contactor “four-pack” configured for testing of a single stage.

METHODOLOGY/EXPERIMENTAL PROCEDURE

SRS Waste Simulant

SRS waste simulant for use in testing was prepared according to a method developed by SRTC personnel for the preparation of "average" SRS supernate simulant (Peterson 2000). The target composition of the average SRS simulant is given in Table 2. Three batches of simulant were prepared. A 1-liter batch was prepared for use in dispersion number measurements, an 8-liter batch was prepared for use in the hydraulic performance testing, and an 8-liter batch was prepared for use in the mass transfer efficiency testing. All simulants were prepared by the INEEL Quality Control Laboratory.

Table 2. Composition of average SRS simulant.

Component	Conc., mol/L	Component	Conc., mg/L
Na	5.6	Cu	1.44
K	0.015	Cr	75
Cs	0.00014	Ru	0.82
OH	2.06	Pd	0.41
NO_3	2.03	Rh	0.21
NO_2	0.50	Fe	1.44
AlO_2	0.28	Zn	8
CO_3^{2}	0.15	Sn	2.4
SO_4^{2}	0.14	Hg	0.05
Cl	0.024	Pb	2.1
F	0.028	Ag	0.01
PO_4	0.007	Tri-n-butyl phosphate (TBP)	0.5
C_2O_4	0.008	Di-n-butyl phosphate (DBP)	25
SiO_3	0.03	Mono-n-butyl phosphate (MBP)	25
MoO_4	0.00007	n-Butanol	2
NH_3	0.001	Formate	1500
		Tri-methylamine (TMA)	10

Optimized CSSX Solvent

The composition of the optimized CSSX solvent used in all testing was 0.007 M BOBCalixC6, 0.75 M Cs-7SB, and 0.003 M TOA in Isopar® L. The solvent was prepared by Peter Bonnesen at ORNL and shipped to the INEEL. Two 5- liter batches of solvent were obtained. Lot 150W had a density of 851.8 ± 0.1 g/L at 25°C as measured at ORNL prior to shipment. This solvent was used as received for measurement of the dispersion number and for all hydraulic performance testing. Lot 190W had a density of 851.8 ± 0.2 g/L at 25°C as measured at ORNL prior to shipment. This solvent was used as received for mass transfer efficiency testing.

Prior to use, quality control distribution coefficient testing was performed on both batches of CSSX solvent using the procedure provided by ORNL. Results of these tests for Lots 150W and 190W are presented in Table 3. All of the distribution coefficients were within 15% of the values measured at ORNL prior to shipment, which was the criterion used for acceptance of the solvent for use.

Table 3. CSSX solvent quality test results.

Contact	D_{Cs} (average of two measurements)	Target D_{Cs}	% of Target
Lot 150W-Extraction	13.6	14.09	96.5
Lot 150W-Scrub	1.27	1.222	103.9
Lot 150W-Strip	0.0261	0.0241	108.3
Lot 190W-Extraction	14.0	14.02	99.9
Lot 190W-Scrub	1.32	1.168	113.0
Lot 190W-Strip	0.0220	0.0195	112.8

Analytical

SRS waste simulant feed samples were submitted for analysis to the INTEC Analytical Laboratory. Aluminum, chromium, copper, iron, molybdenum, lead, palladium, rhodium, ruthenium, silicon, and zinc analyses were performed using Inductively Coupled Plasma Emission Spectroscopy (ICP-ES). Sodium, cesium, and potassium analyses were performed using Atomic Absorption Spectroscopy. Aqueous and organic samples from mass transfer efficiency testing were analyzed by ICP- mass spectroscopy (ICP-MS). Solvent samples were digested in nitric acid in a closed vessel microwave digestion system (CEM model MDS-2100 laboratory microwave with CEM lined digestion vessels) prior to analysis. Additionally, indirect cesium analysis of the solvent samples was performed by stripping the solvent samples several times with dilute nitric acid at an organic to aqueous phase ratio (O/A) of 0.2.

Dispersion Number Measurement

The dispersion number is a measurement of the general ability of a two-phase dispersion to separate (Leonard 1995). A dispersion number greater than 4.4E-04 generally indicates good phase separation in solvent extraction equipment. Dispersion numbers were measured for the extraction, scrub, strip, and sodium hydroxide wash sections of the CSSX flowsheet. Phase volumes proportional to the flow rates of the baseline CSSX flowsheet, as summarized in Table 4, were used for the testing.

Table 4. Relative solution flowrates and O/A ratios.

Section	Stream	Relative Flow	Organic/Aqueous Ratio
Extraction	Solvent Feed	0.333	0.31
	Waste Simulant Feed	1.00	
Scrub	Scrub Feed	0.0667	5.0
Strip	Strip Feed	0.0667	5.0
Wash	Wash Feed	0.0667	5.0

Measured volumes of aqueous and organic solutions, at a phase volume ratio as shown in Table 4 for the section of the flowsheet being tested, were placed into a graduated cylinder. For determining the dispersion number in the extraction section, aqueous solution consisting of SRS waste simulant mixed with 0.05 M HNO_3 scrub solution at a volume ratio of 1 part simulant and 0.067 parts scrub was used. This results in an aqueous solution similar to the extraction section aqueous solution in an operating process where the scrub effluent mixes with the aqueous feed solution. The solution in the graduated cylinder was agitated manually for 20 seconds, agitation was suspended for 10 seconds, and manual agitation was resumed for an additional 20 seconds. The total height of the dispersion and the time required for the dispersion to break were then measured. The criteria used to determine the point at which the dispersion broke was when the interface had returned to its original position and droplets were no longer observed at the interface or in the aqueous or organic phases. Dispersion numbers were calculated according to the equation

$$N_{Di} = \frac{1}{t_b}\sqrt{\frac{z}{g_c}}$$

where t_b is the break time (s), z is the dispersion band height (ft), and g_c is the gravitational constant (32.172 ft/s^2). This process was repeated three times for each flowsheet section.

Hydraulic Performance Testing

The hydraulic performance of a centrifugal contactor is evaluated by measuring the maximum solution throughput (sum of the aqueous and organic flowrates) for which the maximum allowable cross-phase entrainment is not exceeded. Cross-phase entrainment is defined as aqueous solution carryover in the organic effluent stream or organic carryover in the aqueous effluent stream. For the purposes of this testing, two criteria for cross-phase entrainment were used: (1) any observable cross-phase entrainment, as observed by aqueous bubbles or a layer in the bottom of the solvent sample or an organic film or layer on the top of the aqueous sample, and (2) measurement of ≥ 1% cross-phase entrainment.

The maximum throughput was determined for the extraction, scrub, strip and wash sections of the CSSX flowsheet at the baseline O/A ratios, as shown in Table 4, at rotor speeds of 2800 (extraction section only), 3200 rpm, 3600 rpm, 4000 rpm, and 4400 rpm. Additionally, the effect of small changes in aqueous or organic flowrates was evaluated by measuring the maximum throughput at O/A ratios 20% higher and lower than the baseline O/A's.

Testing was performed with the 5.5-cm contactor configured for continuous recycle of the aqueous and organic effluents to the feed vessels. The contactor was started at the speed to be tested. After aqueous flow was initiated and observed exiting the contactor stage, the solvent flow was initiated. After a minimum of three minutes of operation, the aqueous and organic effluent streams were sampled and visually examined for cross-phase entrainment. If cross-phase entrainment was < 1% in both samples, the aqueous and organic feed flowrates were increased incrementally and proportionally. At each new set of flowrates, the samples were examined for cross-phase entrainment after a minimum of three minutes of operation. This process continued until ≥ 1% cross-phase entrainment was measured in either sample. The flowrates at which cross-phase entrainment was first observed and the flowrates at which entrainment was ≥ 1% were recorded. Flowrates were reduced proportionally until cross-phase entrainment was no longer observed, the system allowed to stabilize, and the process repeated until ≥ 1% cross-phase entrainment was measured. This process was repeated for each contactor rotor speed, O/A ratio, and flowsheet section tested.

Mass Transfer Efficiency Testing

Mass transfer efficiency was measured for the extraction and strip section of the CSSX flowsheet using a single stage of 5.5-cm diameter centrifugal contactor. All testing was performed at 3600 rpm and at an O/A of 0.31 for the extraction section and 5.0 for the strip section. For the extraction section, testing was performed at 75% (1,130 mL/min) and 37.5% (565 mL/min) of the maximum throughput determined in the hydraulic performance testing. For the strip section, testing was performed at the throughputs corresponding to the throughputs tested for the extraction section based upon the baseline O/A's of the CSSX flowsheet (321 mL/min and 161 mL/min).

Testing was performed with the 5.5-cm centrifugal contactor configured for once through processing of the feed solutions. Aqueous feed solution consisted of the composition of the aqueous phase in the section of the flowsheet being tested (extraction or strip). For the extraction section, the waste simulant was mixed with 0.05 M HNO_3 scrub at a volume ratio of 1 part simulant and 0.067 parts scrub. This results in an aqueous solution similar to the extraction section aqueous solution in an operating process where the scrub effluent mixes with the aqueous feed solution. Fresh solvent was used for the extraction section testing and solvent effluent from the extraction section was used for the strip section testing (after performing two scrub contacts of the solvent). The contactor was started at a speed of 3,600 rpm. After aqueous flow was initiated and observed exiting the contactor stage, the solvent flow was initiated. The aqueous and organic effluent streams were sampled 2.5 and 5 minutes after the initiation of solvent flow. These operation times correspond to 14 and 28 residence times for the aqueous solution and 7.5 and 15 residence times for the organic solution, which should be adequate to ensure steady state was reached. In order to determine the mass transfer efficiency at a lower throughput, the solvent and aqueous flowrates were reduced by 50% and the aqueous and organic effluent streams were sampled 3 and 6 minutes after the reduction of flowrates. These operation times correspond to 7 and 14 residence times for the aqueous solution and 3.2 and 7.5 residence times for the organic solution, which should be adequate to ensure steady state was reached.

This testing was then repeated for the strip section of the CSSX flowsheet. Prior to performing mass transfer efficiency testing of the strip section, the solvent was scrubbed with 0.05 M HNO_3. Two contacts were performed using the 5.5-cm contactor stage operating at an O/A of 5.0. Mass transfer efficiency testing was then performed for the strip section. The aqueous and organic effluent streams were sampled 2.5 and 5 minutes after the initiation of solvent flow. These operation times correspond to 1.8 and 3.6 residence times for the aqueous solution and 5 and 10 residence times for the organic solution, which should be adequate to ensure steady state was reached. In order to determine the mass transfer efficiency at a lower throughput, the solvent and aqueous flowrates were reduced by 50% and the aqueous and organic effluent streams were sampled 3 and 5 minutes after the reduction of flowrates. These operation times correspond to 1.1 and 1.8 residence times for the aqueous solution and 3 and 5 residence times for the organic solution. These residence times are low, indicating steady state conditions may not have been reached. Typically, three residence times of the aqueous and organic phases will ensure steady state conditions are reached. The short residence times are the result of the volume of solvent available from the mass transfer efficiency testing in the extraction section, which limited the operational time.

Temperature of the solution in the centrifugal contactor was monitored during operation of the mass transfer efficiency testing using a thermocouple which was inserted through the drain line of the contactor. Temperature of the solution was recorded at the time each sample was taken.

In order to calculate the stage efficiency of the centrifugal contactor, a portion of the samples from the mass transfer efficiency tests were re-equilibrated. Sealed vials (50-mL polypropylene centrifuge tubes) containing the aqueous and organic samples were placed in a constant temperature water bath which was set to the temperature at which the samples were originally taken. After equilibrating thermally for at least 15 minutes, aliquots of the samples (at a volume ratio equivalent to the flowrates at which the mass transfer tests were performed) were placed in a clean vial and returned to the water bath. After equilibrating thermally for at least 15 minutes, the vials were agitated for two 20-second intervals with an intermediate 10-second hold period. The vials were returned to the water bath and the phases allowed to separate by gravity. After a minimum of 10 minutes of separation, the samples were centrifuged and returned to the water bath for a minimum of 5 minutes. Samples of the aqueous and organic phases were taken and submitted, along with samples of the original aqueous and organic phases (prior to re-equilibration), for cesium analysis by ICP mass spectrophotometry.

Mass transfer efficiency was calculated as follows, based on the aqueous phase compositions.

$$\eta = \frac{(X - X_{in})}{(X_{eq} - X_{in})} * 100$$

where X is the cesium concentration of the aqueous effluent, X_{in} is the inlet aqueous cesium concentration, and X_{eq} is the cesium concentration of the aqueous effluent after re-equilibration. Aqueous phase concentrations were used for calculation of the efficiency due to the slightly larger uncertainty in the solvent sample analyses resulting from the digestion of the solvent.

The following guide was used for flushing the single stage 5.5-cm centrifugal contactor when preparing for hydraulic or mass transfer efficiency testing of a different section (extraction, scrub, strip, wash) of the CSSX flowsheet.

1) Drain the feed lines and pump by operating the feed pumps in the reverse direction.
2) Drain solution from the centrifugal contactor stage through the drain valve located on the bottom of the contactor stage.
3) Flush a minimum of 5 liters of demineralized water through the contactor stage (while operating) as a preliminary flush of the lines and contactor.
4) Remove the contactor rotor assembly and flush/soak all wetted parts of the assembly using the aqueous solution planned for the next phase of testing (e.g. 0.05 M HNO_3 scrub solution when switching testing from the extraction to scrub section). Continue flushing until the pH of the rinsate is the same as the pH of the rinse solution.
5) Flush all wetted parts of the contactor housing until the pH of the rinsate is the same as the pH of the rinse solution. This includes flushing the adjacent contactor housing through which the aqueous phase exits.
6) Flush the drain lines, samplers, and feed/product vessels until the pH of the rinsate is the same as the pH of the rinse solution.
7) Flush feed lines and pumps until the pH of the rinsate is the same as the pH of the rinse solution.

RESULTS AND DISCUSSION

Dispersion Number Testing

Results of the dispersion number measurements are summarized in Table 5. Dispersion numbers were measured for the extraction, scrub, strip and wash sections of the flowsheet. The dispersion number averaged 1.32E-03 in the extraction section, 6.01E-04 in the scrub section, 8.35E-04 in the strip section, and 3.75E-04 in the wash section. With the exception of the wash section, dispersion numbers were well above the criteria of 4.4E-04 for good separation performance. The average dispersion number of 3.75E-04 obtained for the wash section is slightly below this criterion, indicating a potential difficulty of phase separation in the wash section of the flowsheet. It should be noted that there are inherent inaccuracies in the measurement of the break time when determining the dispersion numbers. The point at which the phases have completely separated is subject to interpretation by the experimenter. In measuring the break time for the wash section, very small aqueous droplets were observed descending through the organic phase for a considerable time after the interface returned to the original position. The end point of the separation of the phases was defined as the point when these aqueous droplets could no longer be observed. As a result, the calculated dispersion number for the wash section is conservative.

Table 5. Dispersion number measurements.

Test Condition	Dispersion Height (ft)	Separation Time (s)	Temperature (°C)	Dispersion Number
Extraction 1	0.509	94	---	1.34E-03
Extraction 2	0.509	96	---	1.31E-03
Extraction 3	0.509	96	25.5	1.31E-03
Scrub 1	0.243	142	---	6.12E-04
Scrub 2	0.243	147	26.9	5.91E-04
Strip 1	0.226	102	24.2	8.22E-04
Strip 2	0.226	99	27.5	8.47E-04
Wash 1	0.207	239	29.1	3.35E-04
Wash 2	0.207	214	26.2	3.75E-04
Wash 3	0.207	193	27.1	4.15E-04

Hydraulic Performance

Maximum throughput as a function of rotor speed was determined for each of the flowsheet sections at the baseline O/A's of the CSSX flowsheet. The results, based upon the first observation of cross-phase entrainment and based upon ≥ 1% cross-phase entrainment, are presented in Figures 4, 5, 6, and 7. Additionally, the maximum throughput was measured for each flowsheet section at O/A's 20% higher and lower than the baseline O/A in order to evaluate the effects of small changes in flowrates during process operation. These results are presented in Figures 8, 9, 10 and 11. Finally, in Figures 12 and 13, the maximum throughputs obtained for the extraction and strip sections are compared to the results obtained in FY-01 at ORNL using a 5.0-cm Costner Industries Nevada Corp. (CINC) centrifugal contactor and the old solvent formulation.

Extraction Section

Maximum throughput for the extraction section ranged from 1245 mL/min at 2800 rpm to 1965 mL/min at 4400 rpm (Figure 4). In all cases of cross-phase entrainment, aqueous phase entrainment in the solvent was observed. Entrainment of the solvent in the aqueous phase was not observed. There is very little difference in maximum throughput for the two throughput evaluation criteria. When cross-phase

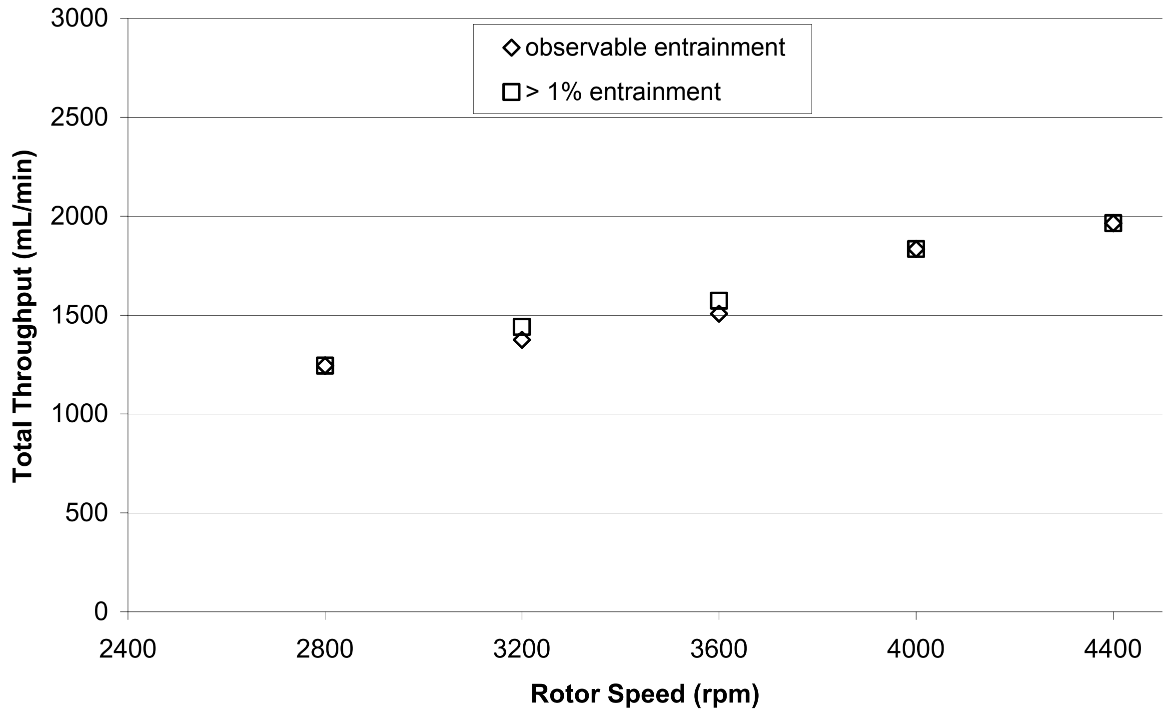

Figure 4. Extraction section maximum throughput at the baseline O/A of 0.31.

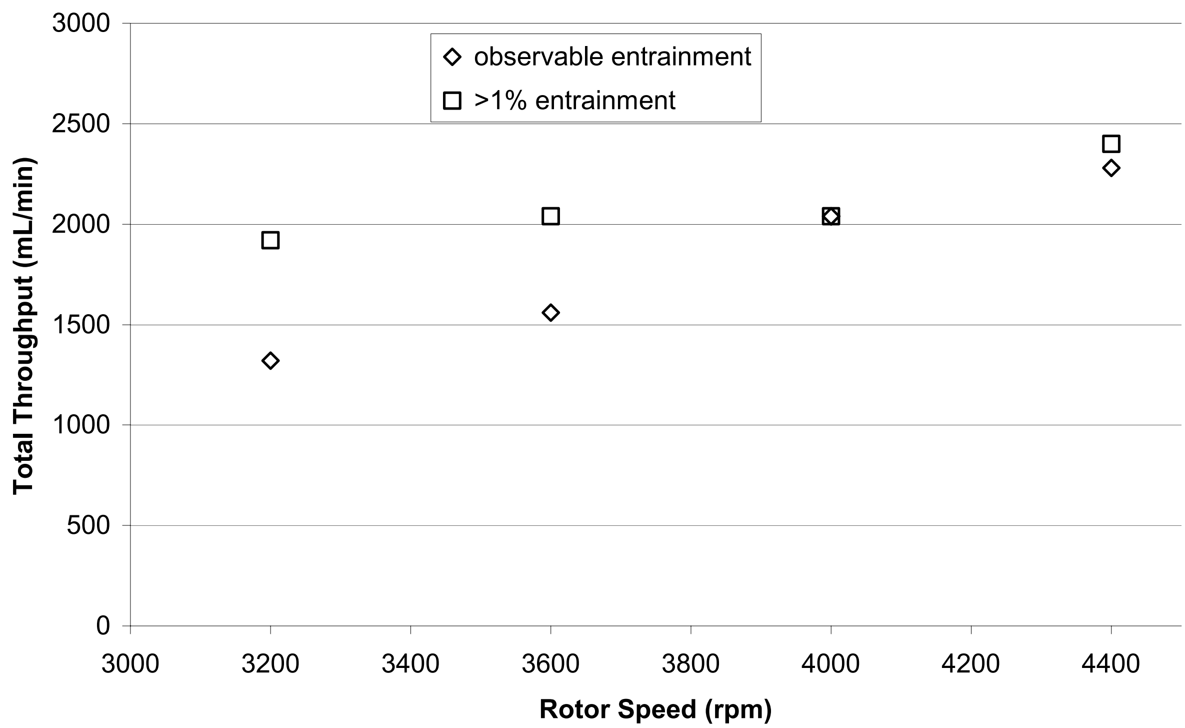

Figure 5. Scrub section maximum throughput at the baseline O/A of 5.0.

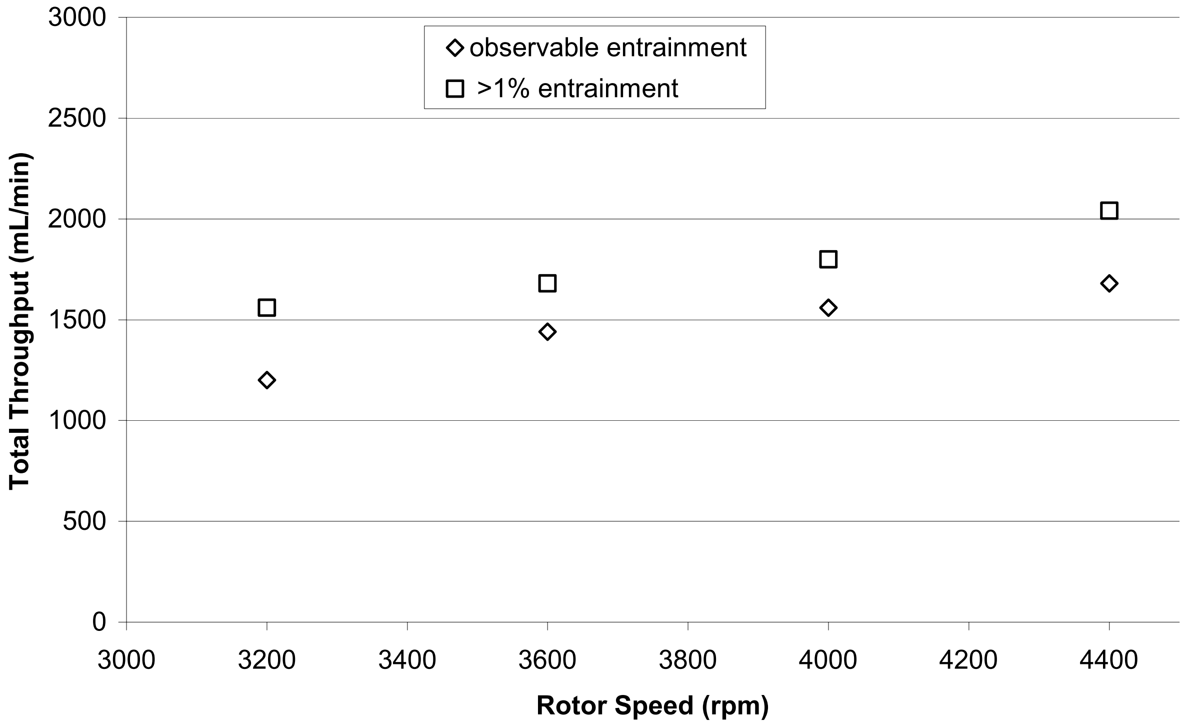

Figure 6. Strip section maximum throughput at the baseline O/A of 5.0.

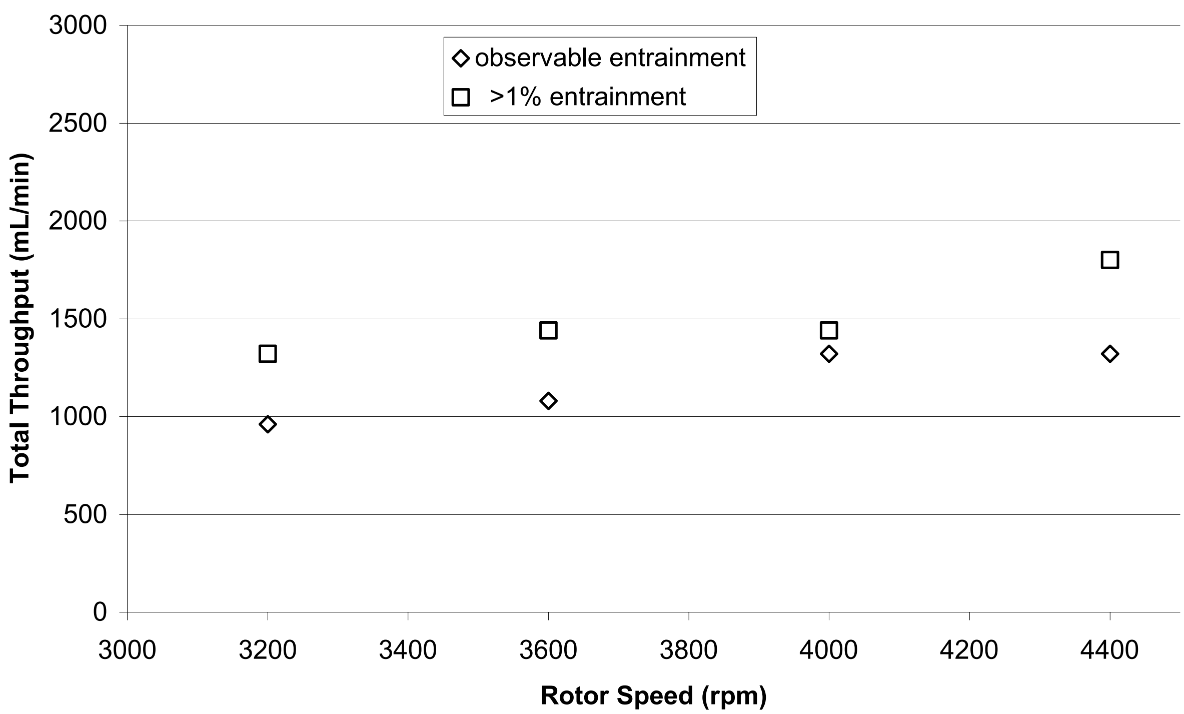

Figure 7. Wash section maximum throughput at the baseline O/A of 5.0.

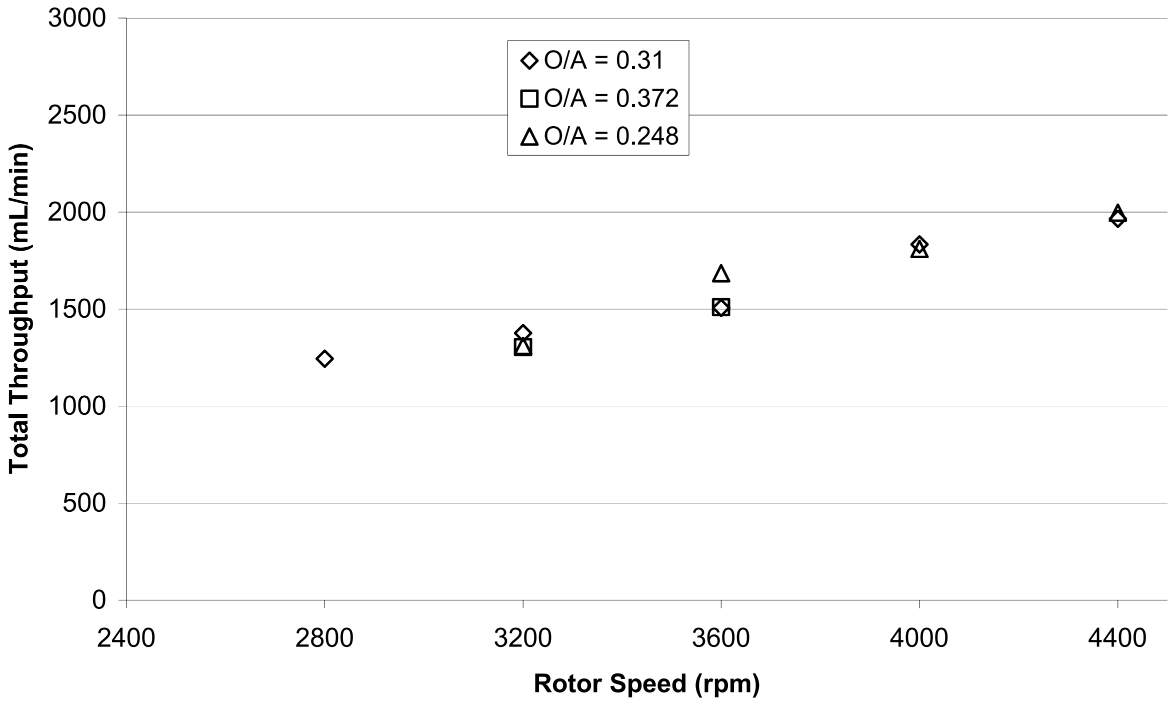

Figure 8. Extraction section maximum throughput as a function of O/A ratio (≥ 1% entrainment).

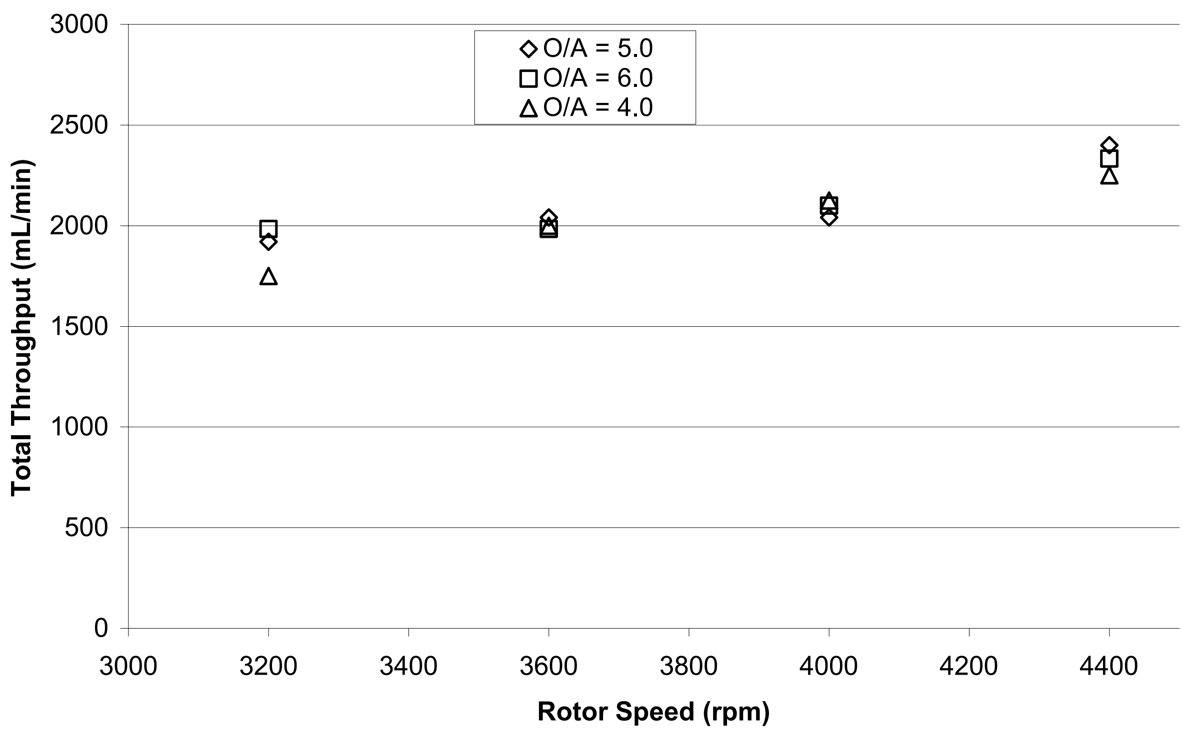

Figure 9. Scrub section maximum throughput as a function of O/A ratio (≥ 1% entrainment).

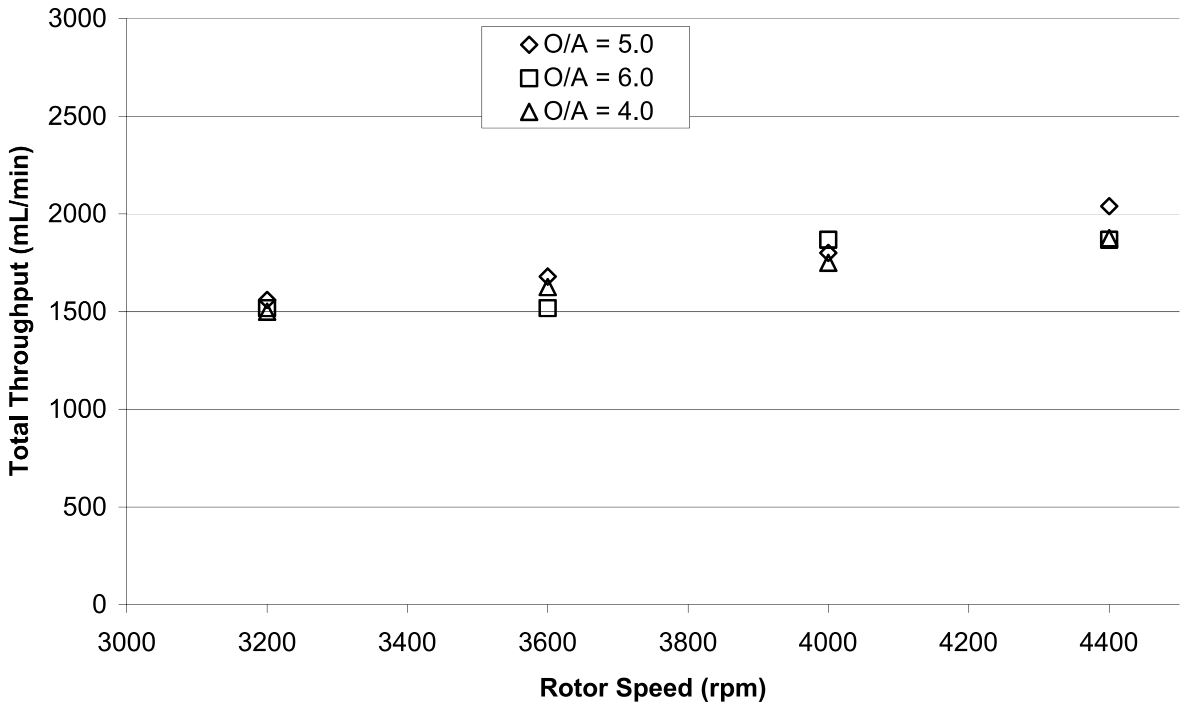

Figure 10. Strip section maximum throughput as a function of O/A ratio (≥ 1% entrainment).

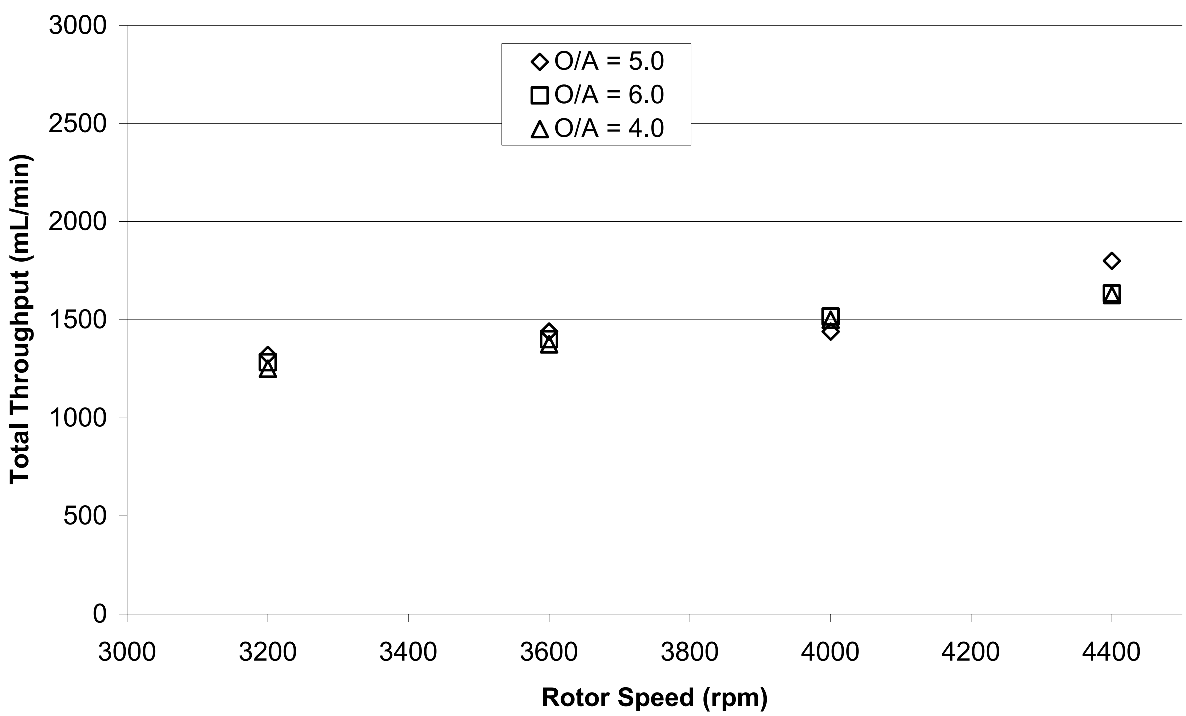

Figure 11. Wash section maximum throughput as a function of O/A ratio (≥ 1% entrainment).

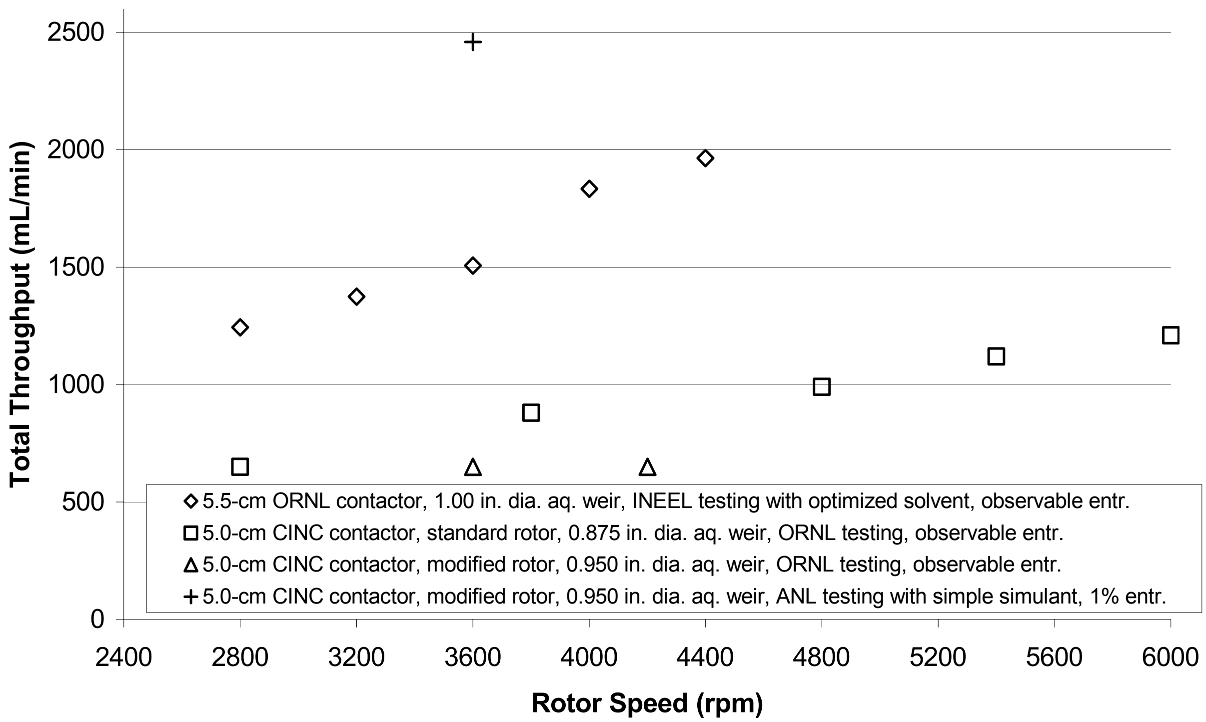

Figure 12. Comparison of extraction section maximum throughput with previous results using the non-optimized solvent.

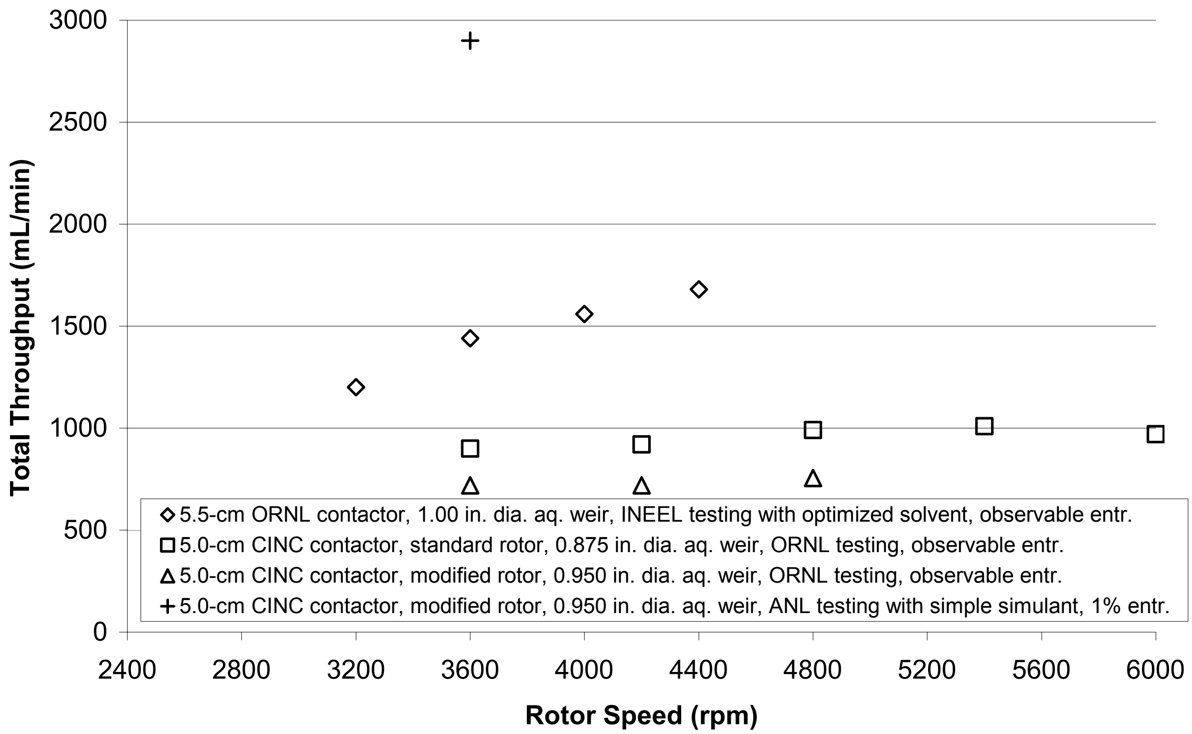

Figure 13. Comparison of strip section maximum throughput with previous results using the non-optimized solvent.

entrainment was first observed, it was typically in amounts ≥ 1%. Maximum throughput was also measured for the extraction section at O/A's 20% higher and lower than the baseline O/A of 0.31 (Figure 8). The maximum throughput is essentially the same at these O/A's indicating that small variations in extraction section process flowrates will not impact the hydraulics of the contactor.

Contactor modeling performed by Argonne National Laboratory (ANL) indicated that the total throughput of the extraction section could be increased without impacting the throughput of the strip section by increasing the radius of the more dense phase weir from 12.7 mm to 13.2 mm. This change was made and hydraulic performance testing was repeated at 4000 rpm. Results were not improved with the larger diameter weir (0.5% cross-phase entrainment at 1703 mL/min and 6% cross-phase entrainment at 1965 mL/min). Additionally, some organic carryover in the aqueous phase was observed at 1703 mL/min total throughput. The original weir was then re-installed and hydraulic testing of the scrub section was initiated.

Scrub Section

The maximum throughput for the scrub section, based on ≥ 1% entrainment, ranged from 1920 mL/min at 3200 rpm to 2400 mL/min at 4400 rpm (Figure 5). The maximum throughput for the scrub section, based on any observable entrainment, ranged from 1320 mL/min at 3200 rpm to 2280 mL/min at 4400 rpm. In all cases of cross-phase entrainment, aqueous phase entrainment in the solvent was observed. Entrainment of the solvent in the aqueous phase was not observed. Maximum throughput was also measured for the scrub section at O/A's 20% higher and lower than the baseline O/A of 5.0 (Figure 9). The maximum throughput is essentially the same at these O/A's indicating that small variations in scrub section process flowrates will not impact the hydraulics of the contactor.

Strip Section

The maximum throughput for the strip section, based on ≥ 1% entrainment, ranged from 1560 mL/min at 3200 rpm to 2040 mL/min at 4400 rpm (Figure 6). The maximum throughput for the strip section, based on any observable entrainment, ranged from 1200 mL/min at 3200 rpm to 1680 mL/min at 4400 rpm. In all cases of cross-phase entrainment, aqueous phase entrainment in the solvent was observed. Entrainment of the solvent in the aqueous phase was typically not observed, with the exception of a few samples in which an organic film was observed on the aqueous phase. Maximum throughput was also measured for the strip section at O/A's 20% higher and lower than the baseline O/A of 5.0 (Figure 10). The maximum throughput is essentially the same at these O/A's indicating that small variations in strip section process flowrates will not impact the hydraulics of the contactor.

Wash Section

The maximum throughput for the wash section, based on ≥ 1% entrainment, ranged from 1320 mL/min at 3200 rpm to 1800 mL/min at 4400 rpm (Figure 7). The maximum throughput for the wash section, based on any observable entrainment, ranged from 960 mL/min at 3200 rpm to 1320 mL/min at 4400 rpm. In all cases of cross-phase entrainment, aqueous phase entrainment in the solvent was observed. Entrainment of the solvent in the aqueous phase was not observed. Maximum throughput was also measured for the wash section at O/A's 20% higher and lower than the baseline O/A of 5.0 (Figure 11). The maximum throughput is essentially the same at these O/A's indicating that small variations in wash section process flowrates will not impact the hydraulics of the contactor.

Comparison of Maximum Throughput to Previous Results with Non-Optimized Solvent

Hydraulic testing was previously performed at ORNL using a 5-cm diameter CINC contactor and the non-optimized solvent formulation (Birdwell and Anderson 2001). Additionally, limited testing was performed at ANL also using a 5-cm diameter CINC contactor and the non-optimized solvent formulation (Leonard et al. 2002). Results obtained using the 5.5-cm diameter ORNL contactor and the optimized solvent are compared to these results in Figures 12 and 13. For the extraction section, throughputs are approximately double those obtained at ORNL using the 5-cm CINC contactor and the non-optimized solvent (INEEL – 1440 mL/min at 3600 rpm, ORNL – 720 mL/min at 3600 rpm). For the testing at the INEEL and at ORNL the maximum throughputs shown were determined based on the first observation of entrainment. At ANL, a maximum throughput of 2460 mL/min was measured at 3600 rpm using a 5-cm CINC contactor and the non-optimized solvent (Leonard et al. 2002). A simplified simulant was used for this testing and the criteria of 1% entrainment was used for determining throughput.

For the strip section, throughputs are also approximately double those obtained at ORNL using the 5-cm CINC contactor and the non-optimized solvent (INEEL – 1506 mL/min at 3600 rpm, ORNL – 650 mL/min at 3600 rpm). At ANL, a maximum throughput of 2900 mL/min was measured at 3600 rpm using a 5-cm CINC contactor and the non-optimized solvent (Leonard et al. 2002). The criteria of 1% entrainment was again used by ANL for determining throughput.

There are several differences in the testing at the INEEL, ORNL and ANL that make a direct comparison of the results difficult. The INEEL used a slightly larger contactor, the design of the contactor used for testing at the INEEL is not identical to the CINC contactor used for the ORNL and ANL testing, and the testing performed at the INEEL was with the optimized solvent. Therefore, differences in maximum throughput can not be directly attributed to the use of the optimized solvent. What can be concluded from this testing is that the maximum throughput of the 5.5-cm diameter ORNL-designed contactor with the optimized solvent is reasonable for this size centrifugal contactor. This conclusion is supported by comparing the results of this testing with the maximum throughput measured for the same 5.5-cm contactor with the PUREX process solvent (for which the contactor was designed). As shown in Figure 14, the total throughput for the PUREX solvent with 0.5 $\underline{M}$ HNO_3 at an O/A of 0.1 ranged from 500 mL/min at 1100 rpm to 2500 mL/min at 4100 rpm. The total throughput for the PUREX solvent with 0.5 $\underline{M}$ HNO_3 at an O/A of 1.0 ranged from 500 mL/min at 1400 rpm to 2000 mL/min at 4100 rpm.

Solvent Density Change During Testing

Previous hydraulic testing at ORNL resulted in a density increase in the solvent from 822.7 to 925.6 g/L at 25ºC (Leonard et al. 2002). The density increase was likely a result of evaporation of the most volatile solvent component, Isopar® L. As a result, the density of the CSSX solvent was closely monitored during testing to ensure the hydraulic performance results would not be affected by a change in density. The change in density of the solvent during INEEL testing is summarized in Table 6. Density changes were minimal, increasing by only 0.33% from the measurement of the density at ORNL until completion of the hydraulic performance tests. This minimal change in solvent density is attributed to the fact that the ORNL-designed contactor does not heat up the solvent significantly during operation. During operation, the solvent remained approximately at ambient temperature. Additionally, the solvent was stored and processed using only Teflon® bottles to prevent any potential solvent losses through the storage bottle and the bottle was kept closed when testing was not in progress.

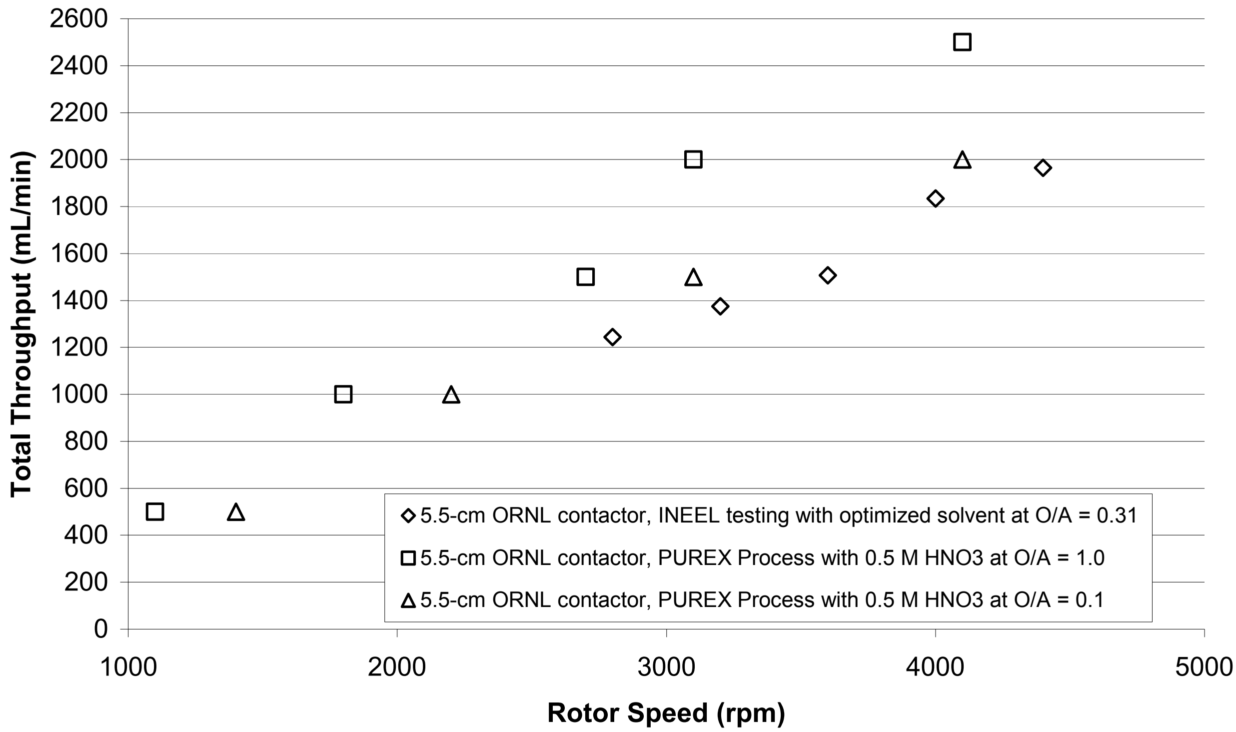

Figure 14. Comparison of maximum throughput in the extraction section with previous results obtained for the PUREX Process.

Table 6. Solvent density measurements during testing.

Time of Measurement	Approximate Cumulative Operating Time (hours)	Density (g/mL)
Prior to shipment to INEEL as measured by ORNL	---	0.8518
Two weeks after receipt as measured by INEEL	---	0.8524
At completion of hydraulic testing of the extraction section	20	0.8533
At completion of hydraulic testing of the scrub section	35	0.8536
At completion of hydraulic testing of the strip section	50	0.8541
At completion of hydraulic testing of the wash section	65	0.8546

Mass Transfer Efficiency

Once the maximum throughputs were determined for each of the flowsheet sections, mass transfer efficiencies were measured at flowrates corresponding to 75% and 37.5% of the maximum throughput in the extraction section. Efficiencies were measured for the extraction and strip sections of the flowsheet. The results of this testing are summarized in Table 7.

Table 7. Mass transfer efficiencies in 5.5-cm diameter contactor operating at 3600 rpm.

Flowsheet Section (operation time)	Total Throughput (mL/min)	Efficiency (%)	Level in Mixing Zone (mm)[1]	Residence Time (s)	D_{Cs} Before Equil.	D_{Cs} After Equil.	Mass Balance (%) Before Equil.	Mass Balance (%) After Equil.
Extraction (2.5 min.)	1,130	73.5	31	1.8	4.8	13.8	105.6	105.4
Extraction (5 min.)	1,130	72.0	31	1.8	4.7	14.8	106.8	106.0
Extraction (3 min.)	565	74.2	---	---	4.8	13.4	111.1	109.7
Extraction (6 min.)	565	74.4	---	---	4.9	13.8	110.9	112.1
Strip (2.5 min.)	321	40.2	13	2.7	0.65	0.14	92.0	93.9
Strip (5 min.)	321	46.5	13	2.7	0.51	0.13	96.3	97.0
Strip (3 min.)	161	36.5	2	0.8	0.65	0.11	100.2	100.2
Strip (5 min.)	161	36.4	2	0.8	0.66	0.11	92.4	99.1

[1]As measured in subsequent testing with 5.5-cm contactor in Plexiglas® housing under the same operating conditions**.**

Extraction Section

Mass transfer efficiencies under extraction section conditions ranged from 72.0% to 73.5% at 75% of the maximum throughput of the contactor and from 74.2% to 74.4% at 37.5% of the maximum throughput of the contactor. Cesium distribution coefficients were determined based on the cesium concentrations in the effluent streams before and after re-equilibration. Before re-equilibration, the distribution coefficient for cesium ranged from 4.7 to 4.9 and after re-equilibration ranged from 13.4 to 14.8. Mass balances for each set of operating conditions were reasonable (105% to112%) and results were consistent for the various sample times and flowrates, indicating sample contamination or analytical error was likely not the cause for the low extraction efficiencies.

Strip Section

Mass transfer efficiencies under strip section conditions ranged from 40.2% to 46.5% at a throughput corresponding to 75% of the maximum throughput in the extraction section (321 mL/min) and from 36.4% to 36.5% at a throughput corresponding to 37.5% of the maximum throughput in the extraction section (160 mL/min). Cesium distribution coefficients were determined based on the cesium concentrations in the effluent streams before and after re-equilibration. Before re-equilibration, the distribution coefficient for cesium ranged from 0.51 to 0.66 and after re-equilibration ranged from 0.11 to 0.14. Again, mass balances for each set of operating conditions were reasonable (92.0% to 100.2%) and results were consistent for the various sample times and flowrates, indicating sample contamination or analytical error was likely not the cause for the low stripping efficiencies.

Additional Testing in Plexiglas® Contactor

Mass transfer efficiencies for the extraction and strip sections were lower than expected. Similar testing performed at ORNL using a 5-cm CINC contactor and the non-optimized solvent yielded mass transfer efficiencies of 86% to 90% for the extraction section and 75% to 100% for the strip section (Birdwell and Anderson 2001). It should be noted that initial mass transfer efficiency test using the "as-received" 5-cm CINC contactor resulted in inadequate efficiencies. Curved vanes in the housing bottom were replaced with straight vanes and the opening in the bottom of the rotor was enlarged from 5.076 to 9.610 mm to convert the rotor from fully to partially pumping. The reported mass transfer efficiencies were obtained after making these modifications.

In order to try and understand the reason for the lower than expected efficiencies, a single stage of 5.5-cm centrifugal contactor in a Plexiglas® housing was setup for testing. This contactor is identical in design to the single stage of the contactor "four-pack" previously tested except the housing is constructed of Plexiglas® which allows solution level to be measured and solution mixing to be observed. A

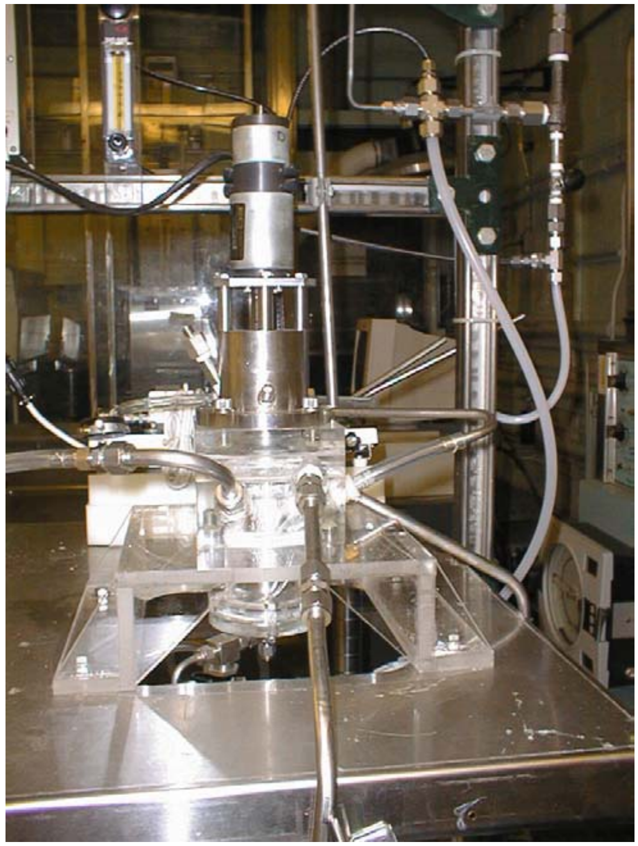

Figure 15. Single stage 5.5-cm centrifugal contactor with Plexiglas® housing.

photograph of this centrifugal contactor is shown in Figure 15. Additional mass transfer efficiency testing was performed using this Plexiglas® contactor.

Initial testing in the Plexiglas® contactor focused on measuring the liquid height in the mixing zone under each of the operating conditions of the mass transfer efficiency testing. The liquid heights, as measured from the bottom edge of the rotor, are presented in Table 7. The liquid level in the mixing zone for the extraction section efficiency testing at 75% of the maximum throughput was 31 mm (1.8 s residence time in the mixing zone). Increasing the rotor speed to 4000 rpm or reducing the rotor speed to 3200 rpm did not result in any measurable change in the liquid level (Table 8). Since these liquid levels appeared to be adequate, it was decided to repeat the mass transfer efficiency testing for the extraction section at 3200 and 4000 rpm in order to determine if the rotor speed affects the mass transfer efficiency.

The liquid heights in the mixing zone for the strip section efficiency testing were 13 mm (2.7 s residence time) at the flowrates corresponding to 75% of the maximum throughput of the extraction section and 2 mm (0.8 s residence time) at the flowrates corresponding to 37.5% of the maximum throughput of the extraction section. With theses low solution levels there was some concern that inadequate mixing was occurring and the residence time in the contactor may be too short. Increasing the total throughput by 50% (481 mL/min) increased the level to 30 mm (4.1 s residence time) and increasing the total throughput by 100% (642 mL/min) increased the level to 38 mm (Table 8). Also, decreasing the rotor speed to 3200 rpm while keeping the total throughput at 321 mL/min increased the level to 19 mm. Decreasing the rotor speed further to 3000 rpm increased the level to 21 mm (4.3 s residence time). Based upon these results, it was decided to repeat the mass transfer efficiency testing for the strip section at the same rotor speed of 3600 rpm but an increased total throughput (481 mL/min), as well as at the original throughput of 321 mL/min but a rotor speed of 3000 rpm. Under both of these conditions, the liquid level is significantly increased.

The results from the mass transfer efficiency tests performed using the Plexiglas® contactor are given in Table 8. For the extraction section, efficiencies of 72.0% and 74.1% were obtained at 3200 and 4000 rpm, respectively. These efficiencies are comparable to the efficiency of 72.0% to 73.5% obtained previously at 3600 rpm, indicating the effect of rotor speed on efficiency is minimal between 3200 and 4000 rpm. The residence time of the solutions in the mixing zone of the contactor was the same for each of the test conditions; therefore, the effect of residence time on the efficiency in the extraction section can not be evaluated. For the strip section, the efficiency decreased slightly from 46.5% to 41.7% when the rotor speed was reduced from 3600 rpm to 3000 rpm at a total throughput of 321 mL/min. With this lower rotor speed, the liquid level in the mixing zone increased from 13 mm to 21 mm (2.7 s and 4.3 s residence time, respectively); however, the solutions may not have been mixed as well. Increasing the contactor total throughput from 321 mL/min to 481 mL/min at the same rotor speed of 3600 rpm resulted in the efficiency increasing from 46.5% to 59.5%. With this change in throughput, the liquid level in the mixing zone was increased from 13 mm to 30 mm and the residence time was increased from 2.7 to 4.1 seconds. At a rotor speed of 3600, the strip section efficiency increased from 36.5% with a residence time of 0.8 s to 46.5% with a residence time of 2.7 s and to 59.5% with a residence time of 4.3 s. With an increased residence time in the mixing zone, there is more time for mixing of the two phases to occur, resulting in an increased efficiency. Further testing would be required to verify if the stage efficiency could continue to be increased by increasing the liquid level and residence time in the contactor.

Table 8. Mass transfer efficiencies using single stage Plexiglas® 5.5-cm diameter contactor.

Flowsheet Section	Total Throughput (mL/min)	Rotor Speed (RPM)	Efficiency (%)	Level in Mixing Zone (mm)	Residence Time (s)
Extraction	1,130	4000	74.1	31	1.8
Extraction	1,130	3200	72.0	31	1.8
Strip	321	3000	41.7	21	4.3
Strip	481	3600	59.5	30	4.1

SUMMARY AND CONCLUSIONS

Maximum throughputs for the CSSX process with the optimized solvent were determined for a 5.5-cm diameter ORNL-designed centrifugal contactor. Throughputs in the extraction section based on 1% cross-phase entrainment ranged from 1245 mL/min at 2800 rpm to 1965 mL/min at 4400 rpm. Throughputs ranged from 1920 mL/min at 3200 rpm to 2400 mL/min at 4400 rpm in the scrub section, 1560 mL/min at 3200 rpm to 2040 mL/min at 4400 rpm in the strip section, and 1320 mL/min at 3200 rpm to 1800 mL/min at 4400 rpm in the wash section. Variations in O/A ratio of 20% had no significant effect on the maximum throughput in any of the flowsheet sections. Maximum throughputs are comparable to the design throughput of the contactor, as well as with throughputs obtained previously in a 5-cm centrifugal contactor with the non-optimized CSSX solvent formulation.

Mass transfer efficiencies of a single stage of 5.5-cm diameter centrifugal contactor have been determined for the extraction and strip sections of the flowsheet. Efficiencies were lower than the process goal of ≥ 80%, ranging from 72 to 75% for the extraction section and from 36 to 47% in the strip section. Additional testing was performed using a single stage of 5.5-cm centrifugal contactor in a Plexiglas® housing so solution levels could be monitored. For the extraction section, variation in the rotor speed from 3200 rpm to 4000 rpm did not have a significant effect on solution levels (31 mm) or mass transfer efficiency. For the strip section, increasing the throughput from 321 mL/min to 481 mL/min increased the level in the mixing zone from 13 mm to 30 mm and resulted in the efficiency increasing from 46.5% to 59.5%.

At this point it is not fully understood why the mass transfer efficiencies are low. Efficiencies could potentially be increased by increasing the mixing intensity and/or the solution level in the mixing zone of the centrifugal contactor (residence time). This would require changes in the design of the contactor. Several methods are available to accomplish this including (1) increasing the size of the opening in the bottom of the rotor, resulting in a contactor which is partially pumping instead of fully pumping, (2) decreasing the number of vanes in the contactor, (3) increasing the vane height, or (4) adding vanes on the rotor and baffles on the housing of the contactor. For the strip section, the flowrates in the 5.5-cm centrifugal contactor are very low as a result of the O/A's of the flowsheet. Increased flowrates resulted in an increase in residence time and stage efficiency. The residence time and stage efficiency could also potentially be increased through the use of a smaller size centrifugal contactor in the strip section operating with the original low flowrates.

The low efficiency results obtained stress the importance of proper design of a centrifugal contactor for use in the CSSX process. A prototype of any centrifugal contactors designed for future pilot-scale or full-scale processing should be thoroughly tested prior to implementation.

REFERENCES

Birdwell and Anderson 2001
J. F. Birdwell and K. K. Anderson, 2001, *Evaluation of 5-cm Centrifugal Contactor Hydraulic and Mass Transfer Performance for Caustic-Side Solvent Extraction of Cesium*, ORNL/TM-2001/137.

Bonnesen et al. 1998
P. V. Bonnesen, L. H. Delmau, T. J. Haverlock, and B. A. Moyer, 1998, *Alkaline-Side Extraction of Cesium from Savannah River Tank Waste using a Calixarene-Crown Ether Structure*, ORNL/TM-13704.

Klatt et al. 2002
L. N. Klatt, J. F. Birdwell, P. V. Bonnesen, L. H. Delmau, L. J. Foote, D. D. Lee, R. A. Leonard, T. G. Levitskaia, M. P. Maskarinec, and B. A. Moyer, 2002, *Caustic-Side Solvent Extraction Solvent-Composition Recommendations*, ORNL/TM-2001/258.

Leonard 1995
R. A. Leonard, 1995, "Solvent Characterization using the Dispersion Number," *Sep. Sci. Technol.*, Vol. 30, pp. 1103-1122.

Leonard et al. 2002
R. A. Leonard, M. C. Regalbuto, S. B. Aase, H. A. Arafat, and J. R. Falkenberg, 2002, *Hydraulic Performance of a 5-cm CINC Contactor for Caustic-Side Solvent Extraction*, ANL-02/18.

Peterson 2000
R. A. Peterson, 2000, *Preparation of Simulated Waste Solutions for Solvent Extraction Testing*, WSRC-RP-2000-361.